80–100 Chromosorb W or a 6-ft 5%-FFAP, 80–100 Chromosorb W column. Product identities were determined by comparison of retention times with those of known compounds and by "mixture VPC tests."

To assure maximum reproducibility, the reactions were carried out in batches of four to eight at a time. The yields of the reaction products were determined from the areas of the peaks which constitute part of the data output of the gas chromatograph. Three standard solutions, having compositions near the approximate value obtained from the reaction mixture, were then prepared for each component and subjected to VPC analysis; the approximate areas were obtained and plotted graphically vs. composition. The actual product compositions were then obtained directly from the graphs.

Detection of Acid Following KCN Reactions. In a control experiment, a solution of diphenyliodonium fluoroborate in dioxene–water was subjected to the conditions specified in Table I for the KCN reactions. No acid could be detected by titration with standard NaOH solution. When the actual reaction with KCN was carried out, the yield of H_3O^+ was found to be 30%.

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Registry No.—Diphenyliodonium fluoroborate, 313-39-3; phenyl-*p*-tolyliodonium fluoroborate, 2665-59-0; *p*-nitrotoluene, 99-99-0; *p*-azidotoluene, 2101-86-2; *p*-cyanotoluene, 104-85-8; *p*-tolyl thiocyanate, 5285-74-5; toluene, 108-88-3; *p*-iodotoluene, 624-31-7.

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(15) The fact that the amount of biphenyl increases sharply when 1,1-diphenylene is present (Table I) suggests that the olefin combines with the phenyl radical to produce a relatively long lived molecule which serves as a reservoir for phenyl radicals. One possible sequence of reactions is the following:

$$(C_6H_5)_2C{=}CH_2 + C_6H_5\cdot \rightleftarrows (C_6H_5)_2\dot{C}CH_2C_6H_5$$

$$(C_6H_5)_2\dot{C}CH_2C_6H_5 + C_6H_5\cdot \rightarrow C_6H_5C_6H_5 + (C_6H_5)_2C{=}CH_2$$

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(17) We have pointed out in a previous paper[3] that ordinarily the material balance in reactions of diphenyliodonium salts with nucleophiles is excellent only when at least 1 equiv of 1,1-diphenylethylene is present in the reaction mixture. Among other effects, the olefin inhibits destruction of iodobenzene by a free-radical chain reaction.

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(28) The direct estimate of the N_3^-/SCN^- reactivity ratio, for example, does not agree well with the indirect estimate with relay via the nitrite ion. This is probably attributable to the fact that the percent error in the determination of the minor component is much greater than that for the major component. For example, the yield of PhN_3 is probably 68 ± 2% and that of PhSCN 5 ± 2% in the appropriate competition reaction cited in Table III. Thus, the N_3^-/SCN^- reactivity ratio might range between 9 and 24 in the direct comparison, and the discrepancy would be magnified in the indirect estimate. However, there is no ambiguity in the given order of reactivities of N_3^-, NO_2^-, and SCN^- toward the diphenyliodonium ion. The reaction with cyanide ion is so complex that its position on the relative reactivity scale must be considered doubtful.

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Mixed Dehydrotrimerization of Biphenyl–Mesitylene by Aluminum Chloride–Cupric Chloride[1a]

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Coupling of biphenyl and mesitylene in the presence of aluminum chloride–cupric chloride provided an oligomer, 2,4,6,2''',4''',6'''-hexamethyl-*p*-quaterphenyl, as the main product. This apparently comprises the first example of dehydrotrimerization of two aromatic substrates to form a mixed product. Mechanistically, the process presumably entails initial formation of a radical cation from biphenyl, which then effects electrophilic attack on mesitylene, followed by fixation of the intermediate to a second mesitylene in a similar sequence of steps. Authentic material was obtained by reaction of mesitylene with *N,N'*-dinitroso-*N,N'*-diacetylbenzidine.

The Ullmann reaction comprises the classical method for joining aromatic nuclei.[2] Biaryls have also been synthesized by other routes involving aryl halides[3] or organometallic compounds.[4] Another approach consists of free-radical arylation.[5] Over the years, a substantial number of reagents have been found which effect dehydrodimerization of aromatic

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Table I. Influence of Variables on Yield in the Biphenyl–Mesitylene Reaction[a]

$CuCl_2$, mol	$AlCl_3$, mol	Biphenyl–mesitylene–$CuCl_2$–$AlCl_3$ (molar ratio)	Time, h	Crude product, g
0.1	0.2	1:3:1:2	2	9[b]
0.1	0.2	1:3:1:2	15	9[b]
0.2	0.4	1:3:2:4	2	10[b]
0.3	0.6	1:3:3:6	2	12[c,d]
0.4	0.8	1:3:4:8	2	13.5[c]

[a] Biphenyl (0.1 mol), mesitylene (0.3 mol), chlorobenzene (120 mL), room temperature. [b] Sticky, dark brown, tar-like mass. [c] Black-green solid which turned to a tar-like mass when dried at 110 °C. [d] Product used for analyses and separation (33% pure 1).

Table II. Ionization[29] and Polarographic[28] Oxidation Potentials

Compd	Registry no.	IP, eV	$E_{1/2}$, V
Biphenyl	92-52-4	8.27	1.48
Mesitylene	108-67-8	8.39	1.53
Benzene	71-43-2	9.24	2.04

Table III. Lowest Energy Absorption Maxima for Donor–Acceptor or Charge-Transfer Complexes[30]

Donor	γ_{max}, cm^{-1}	
	TCNE[a]	Chloranil
Biphenyl	20 000	23 000
Mesitylene	21 700	23 300
Benzene	26 000	29 900

[a] Tetracyanoethylene.

Table IV. Relative Rates of Electrophilic Aromatic Substitution

Compd	Relative rate		pK_B
	Bromination	Nitration	
Mesitylene	1.89×10^8[b]	10^3[c]	0.4
Biphenyl	1.00×10^3[d]	40[e]	5.5
Benzene	1.00	1.0	9.2

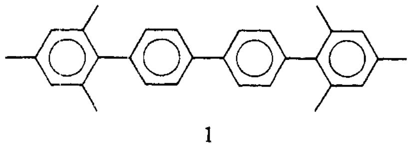
[a] Reference 31, pp 272 and 279. [b] Reference 32. [c] Reference 33. [d] Reference 34. [e] Reference 35.

substrates, including lead(IV) acetate,[6,7] cobalt(III) or manganese(III) trifluoroacetate,[8] cerium(IV) trifluoroacetate,[9] thallium(III) trifluoroacetate,[10] tellerium(IV) chloride,[11] Pd(II) salts,[12] nitric acid,[13] and electrochemical methods.[14] The prior literature[15] most pertinent to our work entails the use of catalyst–oxidant combinations, e.g., aluminum chloride–cupric chloride, ferric chloride, or molybdenum pentachloride. There is only a meager number of previous reports dealing with mixed coupling by dehydrodimerization (or polymerization). These involve use of ferric chloride,[16] lead(IV) acetate,[6,7] and aluminum chloride–cupric chloride.[17,18]

The purpose of the present investigation was to effect mixed coupling of biphenyl and mesitylene and to investigate the mechanistic features.

Results and Discussion

Experimental. Biphenyl and mesitylene were coupled by means of aluminum chloride as catalyst and cupric chloride as oxidant, providing a product which was shown by thin layer chromatography (TLC) to be a complicated mixture. The major component isolated was a trimer-type oligomer, 2,4,6,2''',4''',6'''-hexamethyl-*p*-quaterphenyl (1).



1

Three methods were used for purification. The combination of Soxhlet extraction–chromatography–crystallization was preferred to sublimination or repeated crystallization. A portion of the crude product was extracted first with methanol, then with *n*-pentane, and finally with hexane. In addition to bimesityl, the "dimer" fraction apparently contained isomers of the type p-$C_6H_5C_6H_4C_6H_2(CH_3)_3$ and p-$C_6H_5C_6H_4CH_2C_6H_3(CH_3)_2$, based on mass spectral,[19] IR, and NMR data. 2,4,6-Trimethyl-*p*-terphenyl[7] (2) may be a component. Since the system contains a powerful Lewis acid catalyst, there could well be some rearrangement entailing methyl migration.[20] The major fraction (15–20% yield based on biphenyl) was shown to be 1 from NMR, mass, IR, and UV spectra, similarity to spectral data[21] for 2, and comparison with authentic material. Since the ortho substituents oppose coplanarity of the rings, maximum absorption was observed at 267.5 nm in the UV spectrum, in contrast to the value of 294 nm for *p*-quaterphenyl.[22] This effect is also seen for 2 which exhibited absorption at 248 nm[21] (cf. 276 nm for *p*-terphenyl). An alternate procedure for 1 comprised reaction of mesitylene with *N,N'*-dinitroso-*N,N'*-diacetylbenzidine (<7% yield based on benzidine). This route gave a lower yield, involves more steps, and entails handling of carcinogenic and unstable reagents.

This is the first preparation of 1. Trimer-type products have been observed previously in the oligomerization of biphenyl to form *p*-sexiphenyl[23] and of mesitylene to yield trimesityl.[8] A significant difference is that these cases represent homocoupling whereas compound 1 is derived from the first observed mixed coupling of two different monomers to form a "trimer" (dehydrotrimer). Since inexpensive, readily available starting materials, mild conditions, and relatively uncomplicated techniques are involved, this provides a convenient, one-step synthesis of this novel substance.

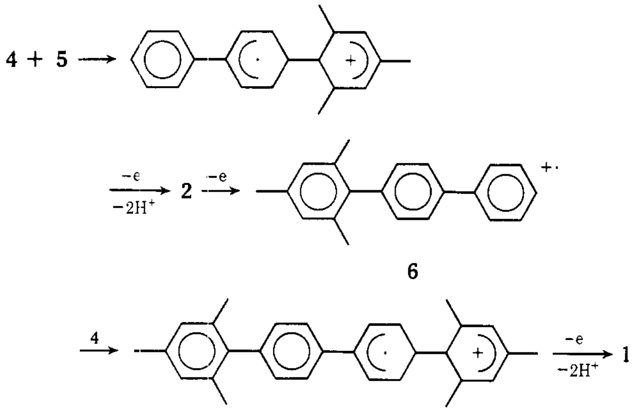
The reaction of biphenyl with mesitylene was investigated in some detail with the aim of determining optimum conditions (Table I).

The reaction was quite sensitive to changes in the amounts of catalyst and oxidant. A biphenyl–mesitylene–$CuCl_2$–$AlCl_3$ molar ratio of 1:3:4:8 gave crude product of highest yield and best appearance; with this molar ratio, hydrogen chloride evolution was most vigorous. Lesser amounts of metal halides produced a lower yield of crude product which was more difficult to purify. Extension of the reaction time to 15 h did not give a higher yield of crude product.

Mechanism. Most of the processes for direct nuclear coupling of aromatic hydrocarbons apparently involve radical cation intermediates, e.g., in the case of aluminum chloride–cupric chloride,[24,25] ferric chloride,[16,26] or molybdenum pentachloride.[27] Various means have been used[28] to measure the ease of organic oxidation entailing removal of an electron, namely, ionization potential (Table II), polarographic oxidation potential (Table II), and lowest energy absorption maxima for donor–acceptor or charge-transfer complexes (Table III). The IP, $E_{1/2}$, and γ_{max} values all indicate that biphenyl (3) should be somewhat more readily oxidized than mesitylene (4). These data, in addition to product distribution, lead to the conclusion that essentially only biphenyl is oxidized to a radical cation, C_6H_5–$C_6H_5^{+\cdot}$ (5). Once 5 is formed, it can interact with a neutral aromatic molecule. From Table IV we note that the rate of electrophilic attack on mesitylene is much larger than for biphenyl. All these data indicate that 5 attacks mesitylene much faster than biphenyl via an electrophilic route, forming 2 (Scheme I). Subsequently, 2 should be oxidized even more easily than biphenyl to form radical cation 6 which can, in turn, become affixed to another mesitylene molecule in a similar sequence to generate the major product 1. Thus 2 apparently serves as precursor of 1. Further oxidative coupling of 2 with another mesitylene molecule would also be favored by the presence of excess alkylbenzene. Note that only very minor amounts (~1% yield) of bimesityl were formed, which comprises additional evidence against generation of mesitylene radical cation to any significant degree.

It should be recognized that disagreement exists concerning the mode of attack by the radical cation upon a neutral aromatic molecule. Nyberg ($FeCl_3$)[16,36] and Kovacic ($AlCl_3$–$CuCl_2$)[24] favor cationic attack whereas Norman et al.[6] [lead(IV) acetate] as well as Mano and Alves[25] ($AlCl_3$–$CuCl_2$) argue that radical involvement occurs.[37] There is only a small difference between biphenyl and mesitylene in relation to

Scheme I



reactivity toward a radical species (relative rate: mesitylene, 6.2; biphenyl, 4.0; benzene, 1.0).[5]

Emphasis should be placed on the fact that aromatic cation radicals are versatile species about which there is much less known than the simpler, more familiar, reactive intermediates. It may be that, depending upon the aromatic substrate and conditions, several processes can occur which produce the same coupled product:[38] (1) reaction of the cation radical with an aromatic molecule (Scheme I); (2) conversion of the cation radical (by loss of an electron) to a dication, followed by combination with an aromatic molecule; or (3) dimerization of cation radicals. The pathway outlined in Scheme I appears to apply most commonly in related situations.[38]

Experimental Section

Materials. Biphenyl (practical) and mesitylene (reagent grade) were obtained from Aldrich Chemical Co., chlorobenzene (99%) from Matheson Coleman & Bell, aluminum chloride (anhydrous powder) from Fisher Scientific Co., and cupric chloride (reagent grade) from Mallinckrodt Chemical Works (dried at 110–120 °C for at least 24 h prior to use). Nitrogen was high purity industrial grade. Alumina (neutral, 80–200 mesh) was supplied by Fisher Scientific Co.

Analytical Procedures. IR spectra were obtained with a Beckman IR-8 spectrophotometer (calibrated with the 1601.8-cm^{-1} band of polystyrene). A Varian T-60 instrument was used to record NMR data which are reported in ppm (δ) (in CCl_4 unless otherwise indicated) relative to tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi RMU-6E (70 eV unless otherwise indicated) and UV spectra with a Cary 17 instrument. Column chromatography was conducted with a Bulcher automatic fraction collector. Melting points (uncorrected) were measured with a Thomas–Hoover capillary apparatus or Berl block. Gas chromatography was performed on an 8 ft, 15% SE-30 on Chromosorb W, column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Procedure. (a) Biphenyl (15.4 g, 0.1 mol), mesitylene (41.8 mL, 0.3 mol), and chlorobenzene (120 mL) were placed in a 250-mL, three-necked flask fitted with a thermometer, gas inlet, stirrer, and condenser, previously flushed with nitrogen. Anhydrous $AlCl_3$ (53.44 g, 0.8 mol) and anhydrous $CuCl_2$ (53.84 g, 0.4 mol) were then added. The reaction mixture was stirred under nitrogen at room temperature for 2 hr during which time it turned purple. The mixture was then poured into 800 mL of ice-cold 6 M HCl and steam distilled. The organic residue was pulverized with water in a blender and washed continuously with 6 M HCl until the wash became colorless and then with water until a negative test ($AgNO_3$) for chloride ion was obtained. The crude product was a black-green solid, yield 13.5 g (88% based on biphenyl).

Product Purification. (a) Extraction–Chromatography–Crystallization. A portion (2 g) of the black-green solid product, from preparation (a), was placed in a Soxhlet apparatus and extracted for 4 h with methanol. Removal of solvent yielded a light-yellow solid which contained mainly biphenyl and bimesityl as determined by ions at *m/e* 154 and 238 in the mass spectrum (10 eV).

Continuous extraction of the methanol-insoluble residue for 6 h with *n*-pentane gave 1.65 g of yellow-brown shiny solid which consisted of a complex mixture. This mixture (1 g) was separated by column chromatography with a 2.5-cm column and 150 g of neutral alumina (diameter/height = 0.06). The eluent was initially petroleum ether (bp 30–60 °C). The polarity of the eluent was gradually increased by the addition of toluene up to 5%. Twenty-minute fractions and a flow rate of 0.6 cm^3/min were used. The progress of the separation was followed by TLC (fraction, wt in g): A, 0.05; B, 0.02; C, 0.04; D, 0.04; E, 0.38; F, 0.03; G, 0.03; H, 0.06; I, 0.04; J (column residue), 0.2.

Fraction A was recrystallized from methanol. Cooling in a methanol–dry ice bath yielded white crystals: mp 42–60 °C; mass spectrum *m/e* 272 (10 eV), 273 (29), 272 (M^+, 100), 271 (11), 257 (40), 242 (26), 241 (23), 215 (17), 167 (29), 165 (20), 149 (77), 113 (20), 104 (17), 85 (29), 83 (26), 71 (49); NMR δ 0.8 (d, impurity), 1.2–1.4 (m, impurity), 1.8 (s), 2.1 (s), 2.5–2.7 (m, impurity), 3.9–4.2 (m, impurity + possible dibenzylic methylene signal at δ 4.0), 6.65 (s, isolated aromatic hydrogens), 6.8 (s, isolated aromatic hydrogens), 7.0–7.6 (m, aromatic hydrogens).

Fraction C was recrystallized from methanol. Cooling in a methanol–dry ice bath yielded white crystals: mp 66–68 °C; mass spectrum *m/e* 272 (10 eV), 273 (33), 272 (M^+, 100), 271 (16), 257 (42), 242 (27), 241 (25), 181 (13), 279 (17), 165 (19), 149 (21), 91 (13), 85 (17), 83 (15), 71 (23); NMR δ 0.81 (d, impurity), 1.2–1.4 (m, impurity), 2.01 (s, 6, *o*-CH_3), 2.29 (s, 3, *p*-CH_3), 2.5–2.7 (m, impurity), 3.9–4.2 (m, impurity), 6.85 (s, 2, $(CH_3)_3C_6\mathbf{H}_2$), 7.10–7.66 (m, aromatic hydrogens).

Fraction E (1) was recrystallized from hexane. Cooling in a methanol–dry ice bath precipitated white needles: mp 233–235.5 °C; a methanol–dry ice bath precipitated white needles: mp 233–235.5 °C; NMR δ 2.01 (s, 12, *o*-CH_3), 2.29 (s, 6, *p*-CH_3), 6.85 (s, 8, $(CH_3)_3C_6\mathbf{H}_2$), and 7.14–7.75 (AB pattern, 8, J = 4 Hz, C_6H_4); mass spectrum *m/e* 390 (10 eV), 391 (29), 390 (M^+, 100), 375 (21), 360 (18), 345 (13), 330 (7), 315 (6), 272 (7), 209 (13), 195 (35), 187 (14), 181 (17), 180 (31), 179 (29), 172 (14), 165 (17), 91 (10); IR (KBr) 1600 (w), 1390 (w), 1370 (w), 1100 (w), 1478 (m), 1000 (m), 845 (m), 817 (s), 742 (w), 734 (w); UV λ_{max} (cyclohexane) 267.5 nm (log ϵ 4.46).

When petroleum ether (bp 30–60 °C) was added to fraction H, an insoluble shiny, white crystalline solid was isolated, mp 283–285 °C. Fractions other than A, C, and E were not examined in detail.

The residue from the previous *n*-pentane extraction was then further extracted with hexane to give 0.23 g of a brown solid which when subjected to TLC (alumina, petroleum ether) showed only one spot with R_f 0.06; this fraction was not investigated thoroughly.

(b) Vacuum Sublimation. Sublimation of preparation (a) at 200–240 °C (0.15–0.1 mm) gave about 30% recovery of material, mp 230–235 °C (crystallized from benzene and then from hexane). The NMR spectrum was the same as that of fraction E.

(c) Repeated Recrystallization. The crude product was extracted with *n*-pentane, and the insoluble residue was extracted with *n*-hexane. The hexane soluble material was repeatedly crystallized from hexane to give a white solid, mp 232–235 °C. The spectral data were identical to those of fraction E.

1 from Benzidine and Mesitylene. *N,N′*-Diacetylbenzidine.[39] A mixture of benzidine (25 g, 0.136 mol) (carcinogenic), 150 mL of acetic acid–acetic anhydride (1:1), and about 0.2 g of zinc powder was refluxed for 20 min. After an additional 100 mL of the acylating mixture was added, reflux was continued for another 20 min. The cooled mixture was added to 700 mL of ice–water and filtered. After the solid was heated in 700 mL of boiling water for 40 min, filtration provided 33.6 g (92%) of amide, mp 332–333 °C (lit.[40] mp 327–330 °C).

***N,N′*-Dinitroso-*N,N′*-diacetylbenzidine.**[41a] A mixture of the amide (33.5 g, 0.13 mol), sodium acetate (21.3 g, 0.32 mol), P_2O_5 (2.5 g), glacial acetic acid (400 mL), and acetic acid (200 mL) was stirred vigorously in an ice bath for 0.5 h. Addition of nitrosyl chloride[41b] (17 g, 0.26 mol) in 50 mL of acetic anhydride during 15 min produced a bright yellow color. After 20 min, the mixture was added to ice-water (1.5 L), filtered (slow process), and dried overnight away from light, yielding a yellow solid, 40 g. In order to effect separation from unchanged or incompletely nitrosated amide, the material was extracted in 1-g portions with chloroform and the solvent was removed as rapidly as possible under vacuum, providing a mustard-colored solid[42,43] (4 g total of crude product): IR (KBr) ~1700 (CO) cm^{-1}; NMR ($CDCl_3$) δ 7.40 (m, AB pattern, 8, ArH), 3.02 (s, 6, CH_3CO).

1 from *N,N′*-Dinitroso-*N,N′*-diacetylbenzidine.[44] The bisnitroso compound was divided into 2-g (0.0063 mol) portions. One part was stirred vigorously with mesitylene (100 mL) for 12 h at 30 °C. The other part was treated similarly for 4 h at 60 °C. After each cooled mixture was filtered from ~0.4 g of solid, mesitylene was removed by distillation and steam distillation. The sticky, red, residual masses were combined in CH_2Cl_2 solvent, since TLC indicated close similarity. Elution through a silica gel column (1 in. × 24 in.) with CH_2Cl_2 provided an orange semisolid (1.1 g) which on stirring with hexane (15 mL) afforded 0.25 g (<7% yield from the bis(nitroso)precursor) of yellow solid, mp 220–230 °C. Preparative TLC (120 mg) on neutral alumina entailing multiple development with hexane followed by extraction with CH_2Cl_2 gave 90 mg of material, mp 235–237 °C. Two crystallizations from benzene-hexane afforded white crystals, mp 236–237 °C.

Anal. Calcd for $C_{30}H_{30}$: C, 92.31; H, 7.69. Found: C, 92.21; H, 7.74.

The IR and NMR spectra were essentially identical to those of the product formed by dehydrotrimerization.

A second fraction, 15 mg, mp 79–82 °C, of slightly higher R_f value, exhibited a molecular ion (*m/e* 272) in the mass spectrum corresponding to the molecular weight of 2 (lit.[21] mp 88–91 °C).

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Registry No.—1, 65879-27-8; $CuCl_2$, 7447-39-4; $AlCl_3$, 7446-70-0; TCNE, 670-54-2; chloranil, 118-75-2; chlorobenzene, 108-90-7; benzidine, 92-87-5; *N,N'*-dinitroso-*N,N'*-diacetylbenzidine, 61444-52-8.

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Rhodium Catalysis of Allylic Oxidations with Molecular Oxygen. β-Silyl-2-cycloalkenones

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Rhodium catalyzed autoxidation of cycloalkenes with allylic carboethoxyl, isopropyl, and trimethylsilyl substituents is examined. Reaction of 3-(trimethylsilyl)cycloalkenes with molecular oxygen in the presence of tris(triphenylphosphine)rhodium(I) chloride is regiospecifc and affords β-silylcycloalken-2-ones in good yields. A new rhodium-catalyzed allylic oxidation reaction is reported which utilizes *tert*-butyl hydroperoxide as oxidizing agent.

Ten years ago, chlorotris(triphenylphosphine)rhodium(I) (1) was shown to catalyze allylic oxidation of olefins[1,2] by molecular oxygen. Cyclohexen-3-one and water are major products of the catalyzed autoxidation of cyclohexene. Since 1 forms coordination complexes with oxygen, it was considered that the catalyst might function by activating molecular oxygen. That is, coordination of oxygen would be prerequisite for catalysis. However, $Rh(CO)(PPh_3)_2Cl$, which interacts only weakly with oxygen, shows similar catalytic activity and product distribution as 1.[3] Furthermore, autoxidations of cyclohexene catalyzed by cobalt(II) carboxylates yield almost identical product mixtures as reactions catalyzed by **1**, and the latter reactions are completely inhibited by 2% of hydroquinone[4a] as is rhodium(I) promoted autoxidation of tetramethylethylene.[4b] These observations suggest that autoxidations catalyzed by **1**, in analogy with cobalt, are free radical chain reactions in which the metal complex initiates chains by inducing decomposition of hydroperoxides. How-

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